

M138

F. R. McCrumb

An Indirect Analytical Methods for  
Mixtures of Lithium, Sodium and  
Potassium



AN INDIRECT ANALYTICAL METHOD FOR MIXTURES  
OF LITHIUM, SODIUM AND POTASSIUM

BY

FRED RODGERS McCRUMB

B. S. Westminster College, 1917

---

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1920



1920  
M138

UNIVERSITY OF ILLINOIS  
THE GRADUATE SCHOOL

June 5 1920

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY  
SUPERVISION BY Fred Rodgers McCrumb  
ENTITLED AN INDIRECT ANALYTICAL METHOD FOR MIXTURES OF  
LITHIUM, SODIUM AND POTASSIUM.  
BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR  
THE DEGREE OF MASTER OF SCIENCE.

J. A. Bralley

In Charge of Thesis

W. L. Noyes

Head of Department

Recommendation concurred in\*

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

Committee

on

Final Examination\*


\*Required for doctor's degree but not for master's

453932



#### ACKNOWLEDGMENT

The writer wishes, at this time, to express his appreciation for the invaluable assistance of Dr. G. McPhail Smith and Dr. S. A. Braley under whose direction this investigation was carried out.



Digitized by the Internet Archive  
in 2013

<http://archive.org/details/indirectanalytic00mccr>



## CONTENTS

|                                      | Page |
|--------------------------------------|------|
| I. PURPOSE OF INVESTIGATION. . . . . | 1    |
| II. HISTORICAL. . . . .              | 1    |
| III. THEORETICAL. . . . .            | 2    |
| IV. EXPERIMENTAL DETAILS. . . . .    | 4    |
| 1. Materials. . . . .                | 4    |
| 2. Method. . . . .                   | 6    |
| V. EXPERIMENTAL DATA. . . . .        | 8    |
| VI. DISCUSSION. . . . .              | 12   |
| VII. CONCLUSIONS. . . . .            | 12   |



## I. Purpose of Investigation.

The determination of alkali metals in mixtures of their salts has long been carried out by a combination of two standard methods. Potassium was determined as the alcohol-insoluble chloroplatinate, lithium by extraction of the combined chlorides with amyl alcohol, and sodium by difference. While these methods give excellent results, the cost of chloroplatinic acid and the tedious procedure incident to an amyl alcohol extraction proved to be rather detrimental factors. This investigation was carried out in the effort to substitute if possible some indirect method which would combine low cost with ease of manipulation and at the same time give results comparable in accuracy with those obtained by the standard method.

## II. Historical.

Lindo (1) determined potassium by adding to a solution containing the chlorides of no metals other than sodium and potassium, sufficient chloroplatinic acid to convert all chlorides to chloroplatinates, evaporating nearly to dryness and after cooling, adding strong alcohol. The sodium salt was dissolved leaving the potassium chloroplatinate which was weighed. Later it was shown that the lithium salt was even more soluble than the sodium chloroplatinate.

Gooch (2) was able to determine lithium by extraction of the alkali chlorides with anhydrous amyl alcohol, the solubilities in grams per hundred cubic centimeter being as follows:

|                    |   |        |
|--------------------|---|--------|
| Potassium Chloride |   | 0.0056 |
| Sodium             | " | 0.0051 |
| Lithium            | " | 6.6000 |





In 1831 Serullas (3) proposed a method for the determination of potassium based upon the fact that potassium perchlorate is practically insoluble in strong alcohol while the perchlorates of sodium and lithium are quite soluble. Owing however to some mistaken ideas regarding the stability of Perchloric acid, this method was abandoned until late years, when other chemists (4) investigated it and found it a very satisfactory method and much less expensive than the chloroplatinic acid procedure.

Various schemes of indirect analysis have been proposed by different chemists but all involving certain algebraical relations in which there have been as many equations as unknown quantities. An example of such is that proposed by Berzelius (5) in 1827, in which a mixture of potassium and sodium chlorides is analyzed by first weighing the total chlorides and then determining the amount of chlorine by precipitation as silver chloride. Later Collier (6) found this method an accurate one for mixtures of pure salts. E. K. Landris (7) has proposed numerous schemes of indirect analysis involving two unknowns, practically all based upon this same principle.

In 1871 R. Bunsen (8) analyzing water for inorganic constituents, worked out a series of indirect methods whereby he was able to determine as high as four unknown quantities. He claimed to have been able to get fairly accurate results through the indirect method.

### III. Theoretical.

Indirect methods of analysis depend upon the fact that when two or more substances are made to undergo the same chemical treat-



ment they either experience a relatively different change of weight or unit weights of each require unequal volumes of a standard solution.

If a mixture of the chlorides of lithium, sodium and potassium be subjected to definite chemical changes, a series of relationships can be established which will lead to a determination of each constituent. In this case, the alkali chlorides are weighed, taken into solution and the chlorine all precipitated as silver chloride. After filtration and removal of excess  $\text{Ag}^+$ , potassium is determined as potassium perchlorate.

If  $X = \text{NaCl}$  and  $A = \text{sum of chlorides}$

$Y = \text{KCl}$   $B = \text{silver chloride}$

$Z = \text{LiCl}$   $C = \text{potassium perchlorate}$

then  $A = X + Y + Z$  and  $Z = A - X - Y$ , but  $Y = \frac{\text{KCl}}{\text{KClO}_4} C = .5381 C$  and

$Z = A - X - .5381 C$ . also  $\frac{\text{AgCl}}{\text{LiCl}} Z + \frac{\text{AgCl}}{\text{NaCl}} X + \frac{\text{AgCl}}{\text{KCl}} Y = B$  or

$$\frac{143.34}{42.40} Z + \frac{143.34}{58.46} X + \frac{143.34}{74.56} Y = B$$

$$3.3809 Z + 2.4520 X + 1.9225 Y = B$$

$$3.3809 Z \pm B - 2.4520 X = 1.9225 Y$$

$$A - X - .5381 C = \frac{B}{3.3809} - \frac{2.4520}{3.3809} X - \frac{1.9225}{3.3809} .5381 C$$

$$A - X - .5381 C = .2958 B - .7253 X - .3060 C$$

$$X - .7253 X = A - .2958 B - .5381 C + .3060 C$$

$$.2747 X = A - .2958 B - .2321 C$$

$$X = \frac{A}{.2747} - \frac{B.2958}{.2747} - \frac{.2321}{.2747} C$$





$$\begin{aligned}
 \text{Therefore } \text{NaCl} &= 3.6403 \text{ A} - 1.0768 \text{ B} - .8449 \text{ C} \\
 \text{KCl} &= .5381 \text{ C} \\
 \text{LiCl} &= \text{A} - (\text{NaCl} + \text{KCl})
 \end{aligned}$$

In any determination in which a co-efficient is used the error tends to be multiplied by such constant. If however the values of such coefficient approaches unity as is the case in all three steps here, the error introduced by calculation should be negligible.

#### IV. Experimental Details.

##### I. Materials:

(a) NaCl - Commercial salt was dissolved in water and the saturated solution filtered through a Buchner funnel. The salt was then precipitated by saturating the solution with pure hydrogen chloride gas, prepared by dropping concentrated sulphuric acid into concentrated hydrochloric acid. The precipitated salt was filtered off and the process repeated. After the second filtration the salt was centrifuged and then dried in a muffle at a dull red heat for some five to six hours.

(b) KCl - The commercial salt was recrystallized three times from a hot aqueous solution, filtered each time through a Buchner funnel, and finally, after being centrifuged, was dried in a muffle at a dull red heat for six hours.

(c) LiCl - Kahlbaum's Lithium Carbonate was used in the preparation of the chloride. Purification was attempted by the  $(\text{NH}_4)_2\text{CO}_3$  method of Stas (9), and also the ether-alcohol-HCl extraction of Rammelsberg (10) but since neither gave results at all satisfactory, the precipitation as lithium fluoride, advocated by



T. W. Richards (11) was substituted and a successful purification carried out. The lithium carbonate was dissolved in pure dilute hydrochloric acid and after treatment with bromine water to oxidize iron, the solution was made slightly ammoniacal and all precipitate filtered off. The bulk of calcium was now removed by addition of ammonium carbonate and filtration. A small amount of ammonium oxalate solution was now added to remove the last trace of calcium. The solution was now concentrated and lithium carbonate precipitated by excess ammonium carbonate. This precipitate was dissolved, after drying in centrifuge, in dilute Nitric acid and concentrated on the steam bath. A solution of ammonium fluoride was prepared by adding hydrofluoric acid to aqueous ammonia in a platinum dish until the solution was only faintly ammoniacal. Excess ammonia was then driven off on the steam bath. The lithium nitrate solution and the ammonium fluoride solution were then poured into a small amount of boiling water in a platinum dish. The precipitated lithium fluoride was washed with hot water and centrifuged. It was then redissolved in nitric acid and the procedure repeated. The lithium nitrate resulting was converted to the chloride by repeated evaporations with hydrochloric acid in a quartz dish. The lithium chloride was freed from excess acid by crystallization from hot aqueous solution several times, finally centrifuged and made up to a definite volume. The spectroscope showed only traces of sodium in this salt, so analysis of the stock solution was carried out by Volhard's method.

(d) HClO<sub>4</sub> - Perchloric acid used was the 20 % acid of commerce having a specific gravity of 1.12.

(e) HCl - Hydrochloric acid was prepared by dropping concentrated sulphuric into a mixture of sodium chloride and concentrated





hydrochloric and after washing with sulphuric absorbing the evolved hydrogen chloride in distilled water.

(f) Alcohol wash liquid for the potassium determination was 95 % ethyl alcohol containing .2 % perchloric acid.

(g) Amyl alcohol was boiled to remove all traces of water.

## 2. Method;

Mixtures of the three chlorides, sodium lithium and potassium in varying proportions were made up and indirect analyses carried out. At first the attempt was made to weigh the mixed chlorides directly but due to the hygroscopic nature of lithium and its tendency to hydrolyze upon drying giving lithium hydroxide, this procedure proved troublesome. Successful drying was accomplished by driving off water in a current of dry hydrogen chloride and removing the excess of that gas by a stream of nitrogen dried by sulphuric. The nitrogen was prepared by gently warming a concentrated solution of sodium nitrate and ammonium chloride. The drying of separate samples by this method required considerable time and care, and it was abandoned in the test runs. Instead, solutions of each salt were made up and carefully analyzed. The samples were then measured out volumetrically using a standard burette for that purpose.

The analysis was carried out as follows:

The weight of the combined chlorides was determined. Their aqueous solution was then made slightly acid with nitric acid and an excess of 10 % silver nitrate added. After boiling, to coagulate the silver chloride, the precipitate was allowed to settle and then filtered through a tared gooch crucible. The precipitate was carefully washed with water made slightly acid with



until Nitric/free from  $\text{Ag}^+$  and then dried in an oven at a temperature of  $130^\circ\text{C}$ , cooled in a desiccator and weighed. After removing the excess  $\text{Ag}^+$  from the filtrate by means of hydrochloric acid and filtration, the solution was evaporated to dryness on the steam bath. The residue was taken up with water, an excess of Perchloric acid added and the solution evaporated to white fumes. A small amount of water was then added and the solution after addition of more perchloric again evaporated to fumes. The residue was then cooled and extracted with the wash alcohol solution, removing excess perchloric acid and all perchlorates present except that of potassium.

The extraction was carried out as follows:

The residue was obtained in a weighed porcelain dish. The alcohol wash was added in small volumes, the residue thoroly macerated after which the extraction liquid was poured through a filter, which retained any foreign matter such as dust etc. The residue was washed with four, five cubic centimeter portions in this manner. The alcohol in excess was then evaporated off, and the residue dissolved in a small amount of hot water. The filter was also washed with hot water and the washings added to the dish. This solution was evaporated to dryness and then dried at  $130^\circ$ , cooled and weighed.

Assuming that :

A = weight of combined alkali chlorides

B = " "  $\text{AgCl}$

C = " "  $\text{KClO}_4$

and using the formulae derived in Part III, the weight of each alkali chloride was calculated.





In order to test the method further, an analysis of Lepidolite, a mineral containing all three of the alkalies, was attempted and the determination of lithium checked up by the Gooch-Amyl alcohol extraction, (2).

The mineral was decomposed by the well-known method of J. Lawrence Smith (12), fusing with calcium carbonate and ammonium chloride in a special crucible. The sintered mass being extracted with boiling water and calcium removed by ammonium carbonate and ammonium oxalate, the analysis of the alkali chlorides was carried out as outlined above, with the exception that the combined chlorides were dried in the special manner to prevent hydrolysis of lithium chloride.

#### V. Experimental Data.

The results obtained are given below: Under A comes the actual weight of each chloride and the weight of the combined chlorides. Under B are given the weights of Silver Chloride, Potassium perchlorate, as determined in the course of analysis, and also the calculated weights of the individual chlorides. The data on the Lepidolite analysis is self-explanatory.

Table 10 shows the error introduced by the presence of salts other than the three alkalies. Small amounts of calcium chloride were introduced and the analyses carried out.



|             |            |             |                            |  |
|-------------|------------|-------------|----------------------------|--|
| 1. A.       |            |             |                            |  |
| <u>NaCl</u> | <u>KCl</u> | <u>LiCl</u> | <u>Total Chlorides (A)</u> |  |
| .1247       | .1266      | .0388       | .2901                      |  |

---

|                 |                             |             |            |             |
|-----------------|-----------------------------|-------------|------------|-------------|
| B.              |                             |             |            |             |
| <u>AgCl (B)</u> | <u>KClO<sub>4</sub> (C)</u> | <u>NaCl</u> | <u>KCl</u> | <u>LiCl</u> |
| .6782           | .2288                       | .1324       | .1231      | .0346       |
| .6798           | .2350                       | .1254       | .1265      | .0382       |
| .6798           | .2342                       | .1261       | .1260      | .0380       |
| .6801           | .2336                       | .1263       | .1257      | .0381       |
| .6800           | .2362                       | .1242       | .1271      | .0388       |

---

2 A.

|             |            |             |                        |  |
|-------------|------------|-------------|------------------------|--|
| <u>NaCl</u> | <u>KCl</u> | <u>LiCl</u> | <u>Total Chlorides</u> |  |
| .1247       | .2532      | .0155       | .3934                  |  |

|             |                         |             |            |             |
|-------------|-------------------------|-------------|------------|-------------|
| B.          |                         |             |            |             |
| <u>AgCl</u> | <u>KClO<sub>4</sub></u> | <u>NaCl</u> | <u>KCl</u> | <u>LiCl</u> |
| .8470       | .4685                   | .1241       | .2521      | .0172       |
| .8464       | .4691                   | .1243       | .2524      | .0167       |
| .8480       | .4695                   | .1222       | .2526      | .0186       |
| .8467       | .4687                   | .1244       | .2522      | .2523       |
| .8466       | .4689                   | .1247       | .0168      | .0169       |

---

3 A.

|             |            |             |                        |  |
|-------------|------------|-------------|------------------------|--|
| <u>NaCl</u> | <u>KCl</u> | <u>LiCl</u> | <u>Total Chlorides</u> |  |
| .2494       | .1266      | .0155       | .3915                  |  |

|             |                         |             |            |             |
|-------------|-------------------------|-------------|------------|-------------|
| B.          |                         |             |            |             |
| <u>AgCl</u> | <u>KClO<sub>4</sub></u> | <u>NaCl</u> | <u>KCl</u> | <u>LiCl</u> |
| .9116       | .2330                   | .2466       | .1254      | .0195       |
| .9072       | .2357                   | .2491       | .1268      | .0156       |
| .9066       | .2352                   | .2502       | .1265      | .0148       |



| <u>AgCl</u> | <u>KClO4</u> | <u>NaCl</u> | <u>KCl</u> | <u>LiCl</u> |
|-------------|--------------|-------------|------------|-------------|
| .9075       | .2348        | .2495       | .1263      | .0150       |
| .9070       | .2351        | .2498       | .1265      | .0152       |

4 A.

| <u>NaCl</u> | <u>KCl</u> | <u>LiCl</u> | <u>Total Chlorides</u> |
|-------------|------------|-------------|------------------------|
| .1247       | .1266      | .0775       | .3288                  |

B.

| <u>AgCl</u> | <u>KClO4</u> | <u>NaCl</u> | <u>KCl</u> | <u>LiCl</u> |
|-------------|--------------|-------------|------------|-------------|
| .8097       | .2350        | .1265       | .1265      | .0758       |
| .8110       | .2345        | .1255       | .1262      | .0771       |
| .8105       | .2355        | .1252       | .1273      | .0763       |
| .8110       | .2354        | .1252       | .1267      | .0769       |
| .8115       | .2352        | .1244       | .1265      | .0779       |

5 A.

| <u>NaCl</u> | <u>KCl</u> | <u>LiCl</u> | <u>Total Chlorides</u> |
|-------------|------------|-------------|------------------------|
| .1247       | .1266      | .1549       | .4062                  |

B.

| <u>AgCl</u> | <u>KClO4</u> | <u>NaCl</u> | <u>KCl</u> | <u>LiCl</u> |
|-------------|--------------|-------------|------------|-------------|
| 1.0730      | .2352        | .1246       | .1265      | .1551       |
| 1.0725      | .2355        | .1248       | .1273      | .1541       |
| 1.0733      | .2349        | .1245       | .1264      | .1553       |
| 1.0731      | .2360        | .1238       | .1270      | .1554       |
| 1.0734      | .2335        | .1257       | .1228      | .1577       |

6 A.

| <u>NaCl</u> | <u>KCl</u> | <u>LiCl</u> | <u>Total Chlorides</u> |
|-------------|------------|-------------|------------------------|
| .0249       | .1266      | .1549       | .3064                  |

B.

| <u>AgCl</u> | <u>KClO4</u> | <u>NaCl</u> | <u>KCl</u> | <u>LiCl</u> |
|-------------|--------------|-------------|------------|-------------|
| .8284       | .2350        | .0248       | .1264      | .1552       |
| .8250       | .2335        | .0297       | .1256      | .1511       |
| .8290       | .2355        | .0237       | .1267      | .1560       |





|             |            |             |                        |
|-------------|------------|-------------|------------------------|
| 7 A.        |            |             |                        |
| <u>NaCl</u> | <u>KCl</u> | <u>LiCl</u> | <u>Total Chlorides</u> |
| .1247       | .0253      | .1546       | .3049                  |

|             |              |             |            |             |
|-------------|--------------|-------------|------------|-------------|
| B.          |              |             |            |             |
| <u>AgCl</u> | <u>KClO4</u> | <u>NaCl</u> | <u>KCl</u> | <u>LiCl</u> |
| .8780       | .0480        | .1239       | .0258      | .1552       |
| .8788       | .0450        | .1257       | .0242      | .1550       |
| .8795       | .0521        | .1189       | .0280      | .1580       |

## 8 Analysis of Lepidolite - Indirect Method.

| No. | <u>Sample</u> | <u>Tot. Chlorides</u> | <u>AgCl</u> | <u>KClO4</u> |
|-----|---------------|-----------------------|-------------|--------------|
| 1.  | .5000         | .2440                 | .5728       | .1728        |
| 2.  | .5000         | .2451                 | .5735       | .1733        |
| 3.  | .5000         | .2446                 | .5730       | .1725        |

|    |             |            |             |
|----|-------------|------------|-------------|
|    | <u>NaCl</u> | <u>KCl</u> | <u>LiCl</u> |
| 1. | .1252       | .0930      | .0262       |
| 2. | .1282       | .0933      | .0236       |
| 3. | .1277       | .0928      | .0241       |

## 9 Analysis of Lepidolite - Gooch Method.

|    |               |               |             |
|----|---------------|---------------|-------------|
|    | <u>Sample</u> | <u>Li2SO4</u> | <u>LiCl</u> |
| 1. | .5000         | .0350         | .0270       |
| 2. | .5000         | .0342         | .0264       |

|             |              |             |                    |                |
|-------------|--------------|-------------|--------------------|----------------|
| 10 A.       |              |             |                    |                |
| <u>NaCl</u> | <u>KCl</u>   | <u>LiCl</u> | <u>Tot. Chlor.</u> | <u>(CaCl2)</u> |
| .1247       | .1266        | .0388       | .2951              | .0050          |
| B.          |              |             |                    |                |
| <u>AgCl</u> | <u>KClO4</u> | <u>NaCl</u> | <u>KCl</u>         | <u>LiCl</u>    |
| .7002       | .2360        | .1206       | .1271              | .0474          |
| .6997       | .2350        | .1220       | .1265              | .0466          |





### Discussion.

Inspection of the various analyses which were carried out will show that the best results were obtained when the substances were present in about the same proportion. Fairly accurate results were obtained however in all proportions using pure salts as long as no one salt was present in very small amounts. As a rule the method was found to work quite well for pure salts, except of course that considerable difficulty was encountered in the drying and weighing of Lithium Chloride, due to its hygroscopic nature and tendency to hydrolyze.

In the general analysis the principal difficulty seemed to be in getting a mixture of alkali chlorides only. Traces of other chlorides influenced the determination considerably and unless very great care was taken to purify the alkali chlorides thoroughly the results were useless. To illustrate this influence a trial analysis was run introducing a small amount of calcium chloride. The results are given in Table 10.

In the analysis of Lepidolite an accurate determination of the alkalies was not attempted. The calcium carbonate was not purified but instead the amount used in fusion was accurately weighed. Since the purpose here was merely to get a comparison, the amount of alkalies found did not represent the content of the mineral.

### Summary

1. An indirect method has been devised which gives accurate results in analysis of pure salts providing no one constituent be present in very small amount.



2. Traces of other salts seriously influence the accuracy of the method. Hence in the analysis of a mineral extreme care is necessary in removing all constituents other than alkali chlorides.
3. Some difficulty is experienced in drying and weighing a mixture of chlorides which contains lithium chloride due to tendency of latter salt to hydrolyze forming lithium hydroxide.
4. In any analysis requiring extreme accuracy it is recommended that the standard method be used unless the substance to be analyzed be a mixture of pure salts.
5. As a means of checking up on an analysis or of making a rapid estimation of alkalies the indirect procedure provides a simple and easily manipulated method.



### Bibliography

1. Lindo, Chem. News 44, 77(1881)
2. Gooch, Am. Chem. Jour. 9, 33, (1887)  
Proc. Am. Acad. Arts and Sci. 22, 177 (1886)
3. Serullas, Ann. Chim. Phys. (2), 294 (1831)
4. Wense, Zeit. Angew Chem. 691, (1891)  
Caspari, ibid 68, 1893
5. Berzelius, De l'analyse des Corps Inorganiques, Paris, 69, 1827.
6. Collier - Am. Jour. Science (2) 37, 344.
7. Landris - J. A. C. S. 17, 466; 18, 182
8. Bunsen - Zeit. fur Anal. Chemie. 10, 391 (1871)
9. Stas - J. A. C. S. 31, 322
10. Rammelsberg, ibid 38, 2326
11. Richards ibid 32, 4-49
12. J. Lawrence Smith- Am. J. Sci. (3) I, 269 (1871)  
Hillebrand - U. S. Geol. Survey, Bull. 422, 171(1910)







UNIVERSITY OF ILLINOIS-URBANA



3 0112 086833602